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(54) CARBON FIBER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a carbon fiber having excellent strength developing properties as a composite material.

SOLUTION: This carbon fiber has wrinkles in the longitudinal direction of the fiber. The maximum depth h (nm) of the wrinkles measured under an interatomic force microscope is $3 < h \leq 100$ and the root mean square surface roughness R_{ms} (nm) measured under the interatomic force microscope is $2 \leq R_{ms} \leq 35$. The value S of the ratio of the actual surface area to the projected area measured under the interatomic force microscope is $1.01 \leq S \leq 1.28$.

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Japanese Patent Laid-Open No. 2003-73932

[Claims for the Patent]

[Claim 1]

A carbon fiber having wrinkles in the lengthwise direction thereof, wherein the maximum wrinkle depth h (nm) measured with an atomic force microscope satisfies the relation that $3 < h \leq 100$, the root-mean-square surface roughness R_{ms} (nm) measured with an atomic force microscope satisfies the relation that $2 \leq R_{ms} \leq 35$, and the ratio S of the real surface area to the projected area measured with an atomic force microscope satisfies the relation that $1.01 \leq S \leq 1.28$.

[Claim 2]

The carbon fiber according to claim 1, wherein the R_{ms} and S , and the total amount A (μg equivalent/g) of the acidic groups, the amount B (μg equivalent/g) of the carboxyl group and the amount C (μg equivalent/g) of the hydroxy group per 1 g of the carbon fiber that are measured by neutralization titration satisfy the following relations:

- i) $25 \leq A \leq 40$, $15 \leq B \leq 30$ and $10 < C \leq 30$ with the proviso that $2 \leq R_{ms} < 20$ and $1.01 \leq S < 1.10$;
- ii) $15 \leq A \leq 30$, $5 \leq B \leq 20$ and $5 < C \leq 15$ with the proviso that $2 \leq R_{ms} < 20$ and $1.10 \leq S \leq 1.28$ or that $20 \leq R_{ms} \leq 35$ and $1.01 \leq S < 1.10$; and
- iii) $0.5 < A \leq 20$, $0 < B \leq 10$ and $0 < C \leq 10$ with the proviso that $20 \leq R_{ms} \leq 35$ and $1.10 \leq S \leq 1.28$.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a carbon fiber, in particular, a carbon fiber in which the surface configuration thereof is physically and chemically controlled.

[0002]

[Conventional Art]

Carbon fibers manufactured from acrylic fibers as precursors have hitherto been utilized in wide ranges as reinforcing fiber materials incorporated in high-performance composite materials for use in applications to aerospace, sports and leisure because such carbon fibers are excellent in mechanical properties. Further grade enhancement is also demanded for carbon fibers as the industrial applications thereof are increasingly being expanded.

[0003]

For the purpose of meeting this demand, it is necessary to control the surface configuration of the carbon fiber and to appropriately control the adhesiveness of the carbon fiber to the sizing agent and the matrix resin.

[0004]

The strength of a composite material is closely related to the surface state of the carbon fiber. In general, a carbon fiber having an extremely smooth surface is inferior in adhesiveness to resin, and cannot attain sufficient strength property when incorporated into a composite; on the other hand, a carbon fiber having large irregularities on the surface thereof attains good adhesiveness to resin, but too prominent irregularities lead to formation of surface defects and such a carbon fiber has a drawback that it is inferior in strength when incorporated into a composite.

[0005]

According to Japanese Patent Laid-Open No. 2000-160436, there is a description that a carbon fiber having a surface area ratio of 1.02 to 1.09 can make the strength and the adhesiveness to resin thereof be compatible with each other at a high level; however, no disclosure has been made on the chemical properties of the surface, in particular, on the amount of oxygen-containing functional groups related to the adhesiveness to the matrix resin. In other words, as matters stand now, there is no supply of a carbon fiber in which a physical configuration such as the irregularities of the surface of a carbon fiber and chemical properties are appropriately controlled for the purpose of attaining the strength of a composite material. Under such circumstances as background, strongly demanded is a carbon fiber excellent in attaining strength as a

composite material by controlling the physical and chemical configurations of the surface of a carbon fiber.

[0006]

[Problems to be Solved by the Invention]

An object of the present invention is to provide a carbon fiber excellent in attaining strength as a composite material by controlling the physical and chemical configurations of the surface of the carbon fiber.

[0007]

[Means for Solving the Problems]

An object of the present invention is to provide a carbon fiber excellent in adhesiveness to a sizing agent and in adhesiveness to a matrix resin by physically and chemically carrying out precise control of the surface state of the carbon fiber.

[0008]

The present invention is a carbon fiber having wrinkles in the lengthwise direction thereof, wherein the maximum wrinkle depth h (nm) measured with an atomic force microscope satisfies the relation that $3 < h \leq 100$, the root-mean-square surface roughness R_{ms} (nm) measured with an atomic force microscope satisfies the relation that $2 \leq R_{ms} \leq 35$, and the ratio S of the real surface area to the projected area measured with an atomic force microscope satisfies the relation that $1.01 \leq S \leq 1.28$.

[0009]

It is preferred that the above described R_{ms} and S , and the total amount A (μg equivalent/g) of the acidic groups, the amount B (μg equivalent/g) of the carboxyl group and the amount C (μg equivalent/g) of the hydroxy group per 1 g of the carbon fiber that are measured by neutralization titration satisfy the following relations:

- i) $25 \leq A \leq 40$, $15 \leq B \leq 30$ and $10 < C \leq 30$ with the proviso that $2 \leq R_{ms} < 20$ and $1.01 \leq S < 1.10$;
- ii) $15 \leq A \leq 30$, $5 \leq B \leq 20$ and $5 < C \leq 15$ with the proviso that $2 \leq R_{ms} < 20$ and $1.10 \leq S \leq 1.28$ or that $20 \leq R_{ms} \leq 35$ and $1.01 \leq S < 1.10$; and
- iii) $0.5 < A \leq 20$, $0 < B \leq 10$ and $0 < C \leq 10$ with the proviso that $20 \leq R_{ms} \leq 35$ and $1.10 \leq S \leq 1.28$.

[0010]

[Embodiments of the Invention]

A carbon fiber the raw material of which is a polyacrylonitrile-based precursor manufactured by a wet or dry method generally has wrinkles in the fiber axis direction due to drawing. It has been known that such wrinkles can attain a good adhesiveness to resin when the carbon fiber is incorporated in a composite material. The present inventors have made an intense study on the maximum wrinkle depth in the axis direction and the adhesiveness to resin for carbon fiber, and consequently have found that the deeper is the maximum wrinkle depth, the better is the adhesiveness to resin. The maximum wrinkle depth as referred to herein means the depth of the deepest wrinkle of a large number of wrinkles. However, contrary, it has been revealed that when the maximum wrinkle depth is larger than 100 nm, the bundling property of the fiber bundle is degraded, and the performance of the composite is degraded due to the degradation of the through-passing ability after a firing step, and further, generation of fluff. Accordingly, the maximum depth of the wrinkles in the fiber axis direction of a carbon fiber is preferably 100 nm or less, more preferably 80 nm or less, and particularly preferably 70 nm or less. On the other hand, when the maximum wrinkle depth is too small, the adhesiveness to resin is degraded and sufficient strength cannot be obtained. Consequently, the effective wrinkle depth capable of providing good adhesiveness to resin is larger than 3 nm, preferably 10 nm or more and more preferably 15 nm or more.

[0011]

For the purpose of attaining the adhesiveness to resin, the ratio of the real surface area to the projected area is set to fall within a range of 1.01 or more and less than 1.28. When the S value is less than 1.01, the surface is perfectly smooth and the adhesiveness to resin is unsatisfactory. When the S value exceeds 1.28, it becomes difficult to attain the compatibility between the strength and the adhesiveness to resin. From such a viewpoint, more preferably the S value is set to fall within a range of from 1.01 or more to 1.27 or less.

[0012]

Further, for the purpose of attaining a sufficient adhesiveness to resin, the root-mean-square surface roughness R_{ms} is set to be 2 nm or more and 35 nm or less. When the root-mean-square surface roughness is less than 2 nm, the adhesiveness to resin is poor in forming a composite and no sufficient strength can be obtained. When the root-mean-square surface roughness is larger than 35 nm, the strength of the composite is degraded.

[0013]

The matters described above are the conditions to be imposed on the carbon fiber for the purpose of fabricating a high-quality composite irrespective as to what the chemical state of the surface of the carbon fiber is. On the other hand, an appropriate control of the surface irregularity, namely, the physical state and the chemical state of the surface of the carbon fiber permits a manufacturing of a further excellent composite.

[0014]

Among the functional groups present on the surface, conceivably there are several groups capable of contributing to the improvement of the performance of the composite. Specific examples of such groups may include acidic functional groups such as a carboxyl group and a phenolic hydroxy group; basic functional groups having a chromene-type structure or a pyrone-type structure; and neutral functional groups such as cyclic oxides. Among these, the acidic groups are particularly preferable because of particularly remarkable advantageous effects. Among such acidic groups, a carboxyl group and a hydroxy group most significantly affect the performance of the composite.

[0015]

Various functional groups have been introduced in surface treatments in conventional methods. However, in the present invention, the carboxyl group and the hydroxy group among these functional groups are independently controlled, and hence advantageous effects that have never been attained in conventional technique can be achieved.

[0016]

As for the amounts of these acidic groups, it is preferable that the total amount A (μ equivalent/g) of the acidic groups satisfies $0.5 < A \leq 40$, the amount B (μ equivalent/g) of the carboxyl group satisfies $0 < B \leq 30$ and the amount C (μ equivalent/g) of the hydroxy group satisfies $0 < C \leq 30$, A, B and C being given in relation to 1 g of the carbon fiber. The total amount of the acidic groups less than the above described range is disadvantageous because of the decrease tendency of the adhesiveness to resin, and the amount concerned larger than the above described range is also disadvantageous because of the decrease tendency of the strength of the carbon fiber. The amount of the carboxyl group and the amount of the hydroxy group preferably fall within the above described ranges, respectively; the above described ranges lead to a result desirable for the compatibility between the strength and the adhesiveness to resin.

[0017]

Further, from the view point of the balance between the physical properties of the surface and the chemical properties of the surface when a composite is formed, Rms, S, A, B and C satisfying the following relations are preferable as far as the oxygen-containing functional groups are concerned because of the high attainment of strength:

- i) $25 \leq A \leq 40$, $15 \leq B \leq 30$ and $10 < C \leq 30$ with the proviso that $2 \leq Rms \text{ (nm)} < 20$ and $1.01 \leq S < 1.10$, namely, the surface wrinkles of the carbon fiber are shallow and scarce and the surface irregularities are scarce;
- ii) $15 \leq A \leq 30$, $5 \leq B \leq 20$ and $5 < C \leq 15$ with the proviso that $2 \leq Rms < 20$ and $1.10 \leq S \leq 1.28$ or that $20 \leq Rms \leq 35$ and $1.01 \leq S < 1.10$, namely, the surface wrinkles of the carbon fiber are moderately deep and the surface irregularities are moderate; or
- iii) $0.5 < A \leq 20$, $0 < B \leq 10$ and $0 < C \leq 10$ with the proviso that $20 \leq Rms \leq 35$ and $1.10 \leq S \leq 1.28$, namely, deep wrinkles are abundant on the surface of the carbon fiber and the surface irregularities are large.

[0018]

By using a carbon fiber the surface configuration of which is physically and chemically controlled as described above, the performance of a carbon fiber composite

material becomes controllable. The surface configuration of a carbon fiber significantly affects the interfacial adhesiveness between the carbon fiber and the matrix resin in a carbon fiber composite material, and the magnitude of the interfacial adhesiveness varies the balance between the performances such as the bending strength and the tensile strength of the carbon fiber composite material. In other words, the control of the surface configuration allows the carbon fiber composite material to have such performance as suitable for the object and application concerned.

[0019]

Further, detailed description will be made on a production method of CF of the present invention in which the physical surface roughness is controlled, on the basis of one example. A production example in which an acrylic precursor produced by wet spinning is used will be described. However, the carbon fiber of the present invention is not limited to such an acrylonitrile-based precursor, but either a rayon-based precursor or a pitch-based precursor can also be used.

[0020]

As the polymerization method of an acrylonitrile-based polymer to be used as a raw material for an acrylonitrile-based precursor fiber, there can be adopted any of the methods well known in the art such as the solution polymerization method and the suspension polymerization method. From the polymer thus polymerized, the unreacted monomers, the residual polymerization catalyst and other impurities are preferably removed as perfectly as possible. The polymerization degree of the polymer is preferably such that the limiting viscosity $[\eta]$ is 1.0 or more and 2.0 or less, from the viewpoint of the drawability in the precursor fiber spinning and the performance attainment of the carbon fiber and the like.

[0021]

Then, a spinning solution is prepared by dissolving the obtained polymer in a solvent. As the solvent, there can be used organic solvents such as dimethylacetamide, dimethylsulfoxide and dimethylformamide, and aqueous solutions of inorganic compounds such as zinc chloride and sodium thiocyanate. However, organic

solvents are preferable because no metals are involved in fibers and the steps can be simplified. Among the organic solvents, dimethylacetamide is most preferable.

[0022]

For the purpose of obtaining a dense coagulated yarn when spinning is carried out, it is preferable to use a polymer solution having a certain polymer concentration or more as the spinning solution; such a polymer concentration is 17% by mass, more preferably 19% by mass or more. Usually, the polymer concentration is preferably 25% by mass or less.

[0023]

As the spinning method, the spinning solution is extruded from the nozzle orifices each having a circular section into a coagulation bath to form a coagulated yarn. The temperature and the concentration of the coagulation bath are appropriately set so that the coagulation bath may provide such conditions that allow the sectional shape of the coagulated yarn to be substantially circular and the taking-up of the coagulated yarn to be carried out with sufficient allowance. Being substantially circular means that no constriction is found in the section and there is included an ellipse having a ratio of the major axis to the minor axis of 1.2 or less, more preferably 1.1 or less. When a precursor fiber having such a sectional shape is used, the flame retarding and carbonization in the firing step are performed uniformly in the direction of the fiber section, and thus a higher-performance carbon fiber can be obtained.

[0024]

As the coagulation bath, an aqueous solution containing the solvent used in the spinning solution is preferably used, and the concentration of the solvent to be contained is appropriately regulated. Such concentration is generally varied depending on the solvent to be used; for example, when dimethylacetamide is used, the concentration thereof is preferably 50 to 80% by mass and more preferably 60 to 75% by mass.

[0025]

As for the temperature of the coagulation bath, the lower temperature is the more preferable; usually the temperature is preferably 50°C or lower; disadvantageously, an

excessively lowered temperature tends to decrease the take-up speed of the coagulated yarn and the productivity tends to be thereby degraded. From such a viewpoint, the temperature of the coagulation bath is more preferably 20°C or higher and 40°C or lower.

[0026]

The above described coagulated yarn is drawn in air at a magnification of preferably 2.0 or less and more preferably 1.3 or less. The lower limit of the drawing magnification in such a drawing in air is 1.0 or more. For the purpose of regulating the indexes of the physical configuration of the surface of the carbon fiber, namely, the maximum wrinkle depth h , the root-mean-square surface roughness R_{ms} and the surface area ratio S so as to fall respectively within the ranges specified in the present invention, the drawing magnification in the drawing in air is preferably set to fall within a range of from 1.0 or more to 2.0 or less. The drawing magnification exceeding 2.0 disadvantageously leads to a tendency that the maximum wrinkle depth as attained by converting into a carbon fiber possibly exceeds 100 nm, a tendency that there is possibly obtained a carbon fiber in which the ratio of the real surface area to the projected area exceeds 1.28, a tendency that the strength as attained by forming a composite is degraded, and the degradation of the through-passing ability in forming the composite and fluff is thereby generated to degrade the strength.

[0027]

Then wet-heat drawing of the coagulated yarn is carried out while the coagulated yarn is washed in boiling water to remove the solvent contained therein. The drawing magnification in this drawing is preferably less than 3 and more preferably 2 or less. The lower limit of the drawing magnification in such wet-heat drawing is 1.0 or more. As the drawing method, it is possible to use a multi-step drawing method involving 2 or more steps. The wet-heat drawing magnification of 3 or more disadvantageously leads to a tendency that the maximum wrinkle depth as attained by converting into a carbon fiber possibly exceeds 100 nm, a tendency that there is possibly obtained a carbon fiber in which the ratio of the real surface area to the projected area exceeds 1.28, and a tendency that the strength as attained by forming a composite is degraded.

[0028]

Further, it is effective to set the temperature of the drawing bath to be as high as possible as long as the mutual bonding of the single fibers does not occur. From this viewpoint, the temperature of the drawing bath is preferably set at a high temperature of 70°C or higher. In the case of a multi-step drawing, the final bath is preferably set at a high temperature of 90°C or higher.

[0029]

The fiber after drawing and washing is subjected to an oiling agent treatment by using a method well known in the art. No particular constraint is imposed on the type of the oiling agent, but an aminosilicone-based surfactant is preferably used.

[0030]

After the oiling agent treatment, drying and densifying are carried out. As for the temperature for the drying and densifying, the drying and densifying are needed to be carried out at a temperature exceeding the glass transition temperature of the fiber, but the temperature concerned possibly varies from a water-containing state to a dry state, and preferred is a method wherein a roller heated to temperatures of from about 100 to 200°C is used.

[0031]

After drying and densifying, a post-drawing is carried out. The post-drawing can adopt various methods such as a dry heat drawing using a high-temperature heated roller, a platen pin or the like and a steam drawing using pressurized steam. The drawing magnification is 1.1 or more, and more preferably 2.0 or more.

[0032]

Such an acrylic precursor fiber is made to pass through a hot air flame retarding furnace set at 220 to 270°C and a flame retarded fiber can thereby obtained. The drawing magnification in the post-drawing step is selected so that the predetermined drawing magnification may be attained, as a whole, both by the pre-drawing step consisting of the drawing in air and the wet-heat drawing carried out before the drying and densifying and by the post-drawing step carried out after the drying and densifying. Various oxidative atmospheres such as the atmospheres of air, oxygen, nitrogen

dioxide and hydrogen chloride can be adopted for the atmosphere in the flame retarding step, but the air atmosphere is preferred because of low cost.

[0033]

The flame retarded fiber obtained as described above is carbonized in an inert atmosphere such as a nitrogen atmosphere. From the viewpoint of attaining the strength of the carbon fiber, it is preferable to carry out the carbonization at a temperature of 1900°C or lower, and the lower limit is 1000°C and preferably 1200°C.

[0034]

Next, description will be made on a method for obtaining a carbon fiber the surface state of which is chemically controlled. The carbon fiber can be enhanced in the affinity and the adhesiveness to the matrix resin in a composite material by introducing oxygen-containing functional groups into the carbon fiber with the aid of application of the electrolytic oxidation treatment to the carbon fiber in an electrolytic solution or with the aid of application of an oxidation treatment to the carbon fiber in a vapor phase or in a liquid phase.

[0035]

Here, description will be only made on the electrolytic oxidation treatment in nitric acid because this treatment permits a short time oxidation treatment and an easy control of the oxidation treatment. However, the oxidation treatment is not limited to the electrolytic oxidation treatment in nitric acid from the viewpoints of the electrolyte and the treatment method, but may be carried out by any other method well known in the art.

[0036]

There can be adopted either an acidic or an alkaline electrolytic solution for the electrolytic oxidation treatment. Examples of the electrolyte to be dissolved in an acidic electrolytic solution may include inorganic acids such as sulfuric acid and nitric acid; organic acids such as acetic acid and butyric acid; and salts such as ammonium sulfate, ammonium nitrate and ammonium hydrogen sulfate. Preferably used among these are sulfuric acid and nitric acid that exhibit strong acidity. Examples of the electrolyte to be dissolved in an alkaline electrolytic solution may include hydroxides

such as sodium hydroxide and potassium hydroxide; ammonia; inorganic salts such as sodium carbonate and sodium hydrogen carbonate; organic salts such as sodium acetate and sodium benzoate; potassium salts, barium salts and other metal salts and ammonium salts of these; and organic compounds such as tetraethylammonium hydroxide and hydrazine. From the viewpoint of preventing the curing failure of the resin, preferably used among these are ammonium carbonate, ammonium hydrogen carbonate and tetraalkylammonium hydroxides, which do not contain any alkali metal. The concentration of the electrolyte to be used is preferably 1% by mass or more and 50% by mass or less. For the purpose of controlling the total amount of the acidic groups, the amount of the carboxyl group and the amount of the hydroxy group, it is possible to arbitrarily use a mixture of two or more of these electrolytic solutions.

[0037]

Further, the treatment temperature preferably falls within a range from 15°C to 80°C because the treatment temperature affects the control of the amount of the functional groups.

[0038]

The current value and the application time of current in the electrolysis treatment vessel, namely, the electric charge to be used also affects the production amount of each of the individual functional groups.

[0039]

The electric charge to be used can be optimized according to the carbonization degree of the carbon fiber and the type and concentration of the salt to be used. From the viewpoint of appropriately suppressing the degradation of the crystallinity of the surface layer, such electric charge is set to fall within a range preferably from 3 to 500 coulomb/g and more preferably from 5 to 200 coulomb/g.

[0040]

After the electrolytic oxidation treatment, it is desired to wash with water and dry the yarn. In drying, when the temperature is too high, the functional groups present on the outermost surface of the carbon fiber tend to vanish due to thermal decomposition.

Thus, the drying temperature is preferably set to be as low as possible, and the drying is desired to be carried out at 200°C or lower.

[0041]

By combining, with an ordinary method, a carbon fiber obtained by such a method as described above with a matrix, there can be produced a prepreg that is an intermediate base material or a composite material that is a final product. No particular constraint is imposed on the resin to be used as the matrix. However, examples of the resin to be used as the matrix may include epoxy resin, phenolic resin, polyester resin, vinyl ester resin, bismaleimide resin, polyimide resin, polycarbonate resin, polyamide resin, polypropylene resin and ABS resin. Alternatively, in addition to the above described resins, cement, metals, ceramics and the like can also be used for the matrix.

[0042]

[Examples]

Hereinafter, more specific description will be made on the present invention with reference to Examples. It is to be noted that individual physical property values were measured by the methods described below. In each of the measurements, a plurality of samples were evaluated and the average value derived therefrom was adopted.

[0043]

It is also to be noted that “%” used for representing a content means “% by mass.”

[0044]

<Wrinkle depth>

A few single carbon fibers to be evaluated were placed on a hemocover glass. The both ends of each single fiber were fixed with a liquid adhesive (for example, correcting fluid, which is stationery) to prepare a sample. Measurement was made for the sample using an atomic force microscope (SPI3700/SPA-300 manufactured by Seiko Instruments, Inc.) and a cantilever, DF-20, made of silicon nitride, in a cyclic contact mode. The measurement was conducted for a randomly selected range of 2.5 μm of each single carbon fiber. The measurement image obtained was subjected to two-dimensional Fourier transformation; the low-frequency component corresponding to

the curvature of carbon fiber surface, namely, moderate irregularity deformation was rejected; and then, inverse transformation was made to remove the irregularities due to the curvature of the surface of the carbon fiber. The image obtained by applying inverse Fourier transformation to the plane image obtained by applying the above described treatment suffers some distortions due to mathematical treatment on the upper and lower edges and the right and left edges of the image. Therefore, from the central portion of the image, a 2 μm square of image was taken out, and the depth of each of the displayed wrinkles in an arbitrary section was measured. The deepest wrinkle of a plurality of wrinkles present on the surface of each of the single carbon fiber obtained by the above described measurement method was defined as "the maximum depth wrinkle."

[0045]

<Root-mean-square surface roughness>

The original image obtained by the above described method with an atomic force microscope was subjected to two-dimensional Fourier transformation; the low-frequency component corresponding to the curvature of the surface of the carbon fiber was rejected; and then, inverse transformation was made to remove the component originated from the curvature of the surface of the carbon fiber and thus the steep wrinkle shapes were exclusively displayed. From the image thus obtained, the root-mean-square surface roughness was measured with the aid of a software, in a cross section mode, adjunct to the apparatus.

[0046]

<Ratio of the real surface area to the projected area: Surface area ratio>

The original image obtained by the above described method with an atomic force microscope was subjected to two-dimensional Fourier transformation; the low-frequency component corresponding to the curvature of the surface of the carbon fiber was rejected; and then, inverse transformation was made to remove the component originated from the curvature of the surface of the carbon fiber and thus the steep wrinkle shapes were exclusively displayed. From the image thus obtained, the ratio of

the real surface area to the projected area, namely, the surface area ratio was measured with the aid of a software, in a cross section mode, adjunct to the apparatus.

[0047]

<Total amount of the acidic groups, the amount of the carboxyl group and the amount of the hydroxy group>

Three samples of approximately 1.3 g of carbon fiber were soaked in three types of alkaline solutions each in an amount of 80 ml for 24 hours in an atmosphere of nitrogen. The supernatant liquid of each of the alkaline solutions was collected and filtered with a 5 μm disc filter. By using 20 ml of the filtrate of each of the alkaline solutions, potentiometric titration was carried out with a 10 mmol/l hydrochloric acid. The potentiometric titration was carried out with an apparatus, COM-550, manufactured by Hiranuma Sangyo Corporation. A blank measurement without using a carbon fiber was also carried out at the same time, and a surface functional group amount was derived from the following equation. For each evaluation, three measurements were carried out and the average value derived therefrom was adopted.

[0048]

CF surface functional group amount (μ equivalent/g) = {(titer (ml) for a sample – titer (ml) for a blank sample) \times 10 \times alkaline solution concentration (mol/l) \times f \times 80/20 \div weight of used carbon fiber (g)} \times 1000

wherein:

f: Factor for a 0.01 N hydrochloric acid (10 mmol/l hydrochloric acid for volumetric analysis manufactured by Kishida Chemical Co., Ltd. was used; 1.00 at 20°C).

The alkaline solutions to be used and the surface functional group(s) to be analyzed are as follows:

- 10 mmol/l sodium hydroxide \rightarrow carboxyl group + carboxyl group derived from lactone ring opening + hydroxy group
- 5 mmol/l sodium carbonate \rightarrow carboxyl group + carboxyl group derived from lactone ring opening
- 10 mmol/l sodium hydrogen carbonate \rightarrow carboxyl group

Accordingly, the total amount of the acidic groups on the surface is derived from the titer of sodium hydroxide, and the amount of the carboxyl group is derived from the titer of sodium hydrogen carbonate. The amount of the hydroxy group is derived from “the surface functional group amount derived from the titer of sodium hydroxide” – “the surface functional group amount derived from the titer of sodium carbonate.”

[0049]

<Interfacial shear strength>

The interfacial shear strength as an evaluation of the adhesion strength to resin was evaluated by the single fiber embedding (fragmentation) method. For example, a specific description is found in “Development and Evaluation Method of Carbon Fiber,” published by Realize Ltd., pp. 157 to 160. Specifically, there was prepared a test piece in which a single fiber was embedded in a resin, and an elongation larger than the fracture elongation of the fiber was imparted to the test piece. By measuring the length of each of the fiber broken in the resin, the interfacial shear strength was derived.

[0050]

Critical fiber length (mm) = $4 \times \text{average fiber length (mm)} / 3$

Interfacial shear strength (MPa) = $\text{fiber strength (MPa)} \times \text{fiber diameter (mm)} / 2 \times \text{critical fiber length (mm)}$

The resin used for preparation of the test piece was obtained by mixing 100 parts of “Araldite CY230” with 35 parts of “hardener HY2967”, manufactured by Ciba Geigy Corp.; casting the mixture into a purpose-built mold, and curing it under the temperature conditions of 20°C for 24 hours and 60°C for 6 hours. The tensile test was carried out at room temperature. An elongation was imparted to the test specimen within a range (an elongation of 7%) in which the test piece was not broken, and then the length of each of the broken fibers in the resin was measured with a polarization microscope to derive the average fiber length.

[0051]

<Strand strength>

The strand strength was measured according to the method described in JIS R-7601.

[0052]

A strand was prepared as follows: "Epicoat 828" (100 parts) manufactured by Yuka-Shell Co., Ltd., methyl nadic anhydride (90 parts), dibenzyl dimethylamine (2 parts) and acetone (50 parts) were mixed together to prepare a resin; this resin having such a composition as described above was impregnated into a carbon fiber; and was cured under the conditions that curing was made at 50°C for 1 hour, then the temperature was increased to 130°C over a period of 1 hour, and then curing was made at 130°C for 2 hours, to yield a resin-impregnated strand. By using the obtained resin-impregnated strand, the resin-impregnated strand tensile strength was obtained according to the resin-impregnated strand test method (in conformity with JIS R 7601).

[0053]

Hereinafter, description will be made on Examples and Comparative Examples, and various data are summarized in Table 1.

[0054]

(Example 1)

An acrylic copolymer obtained by copolymerizing acrylonitrile (96%), methacrylic acid (1%) and acrylamide (3%) by the suspension polymerization method was dissolved in dimethylacetamide to prepare a spinning solution (the polymer concentration: 21%, the spinning solution temperature: 60°C). By using a spinneret that had an orifice diameter of 0.075 mm and the number of orifices of 3000, the spinning solution was extruded into a 67% aqueous solution of dimethylacetamide set at 38°C to yield a coagulated yarn.

[0055]

The coagulated yarn was subjected to drawing in air and then wet-heat drawing, respectively, at the magnifications shown in Table 1. The magnifications in the drawing in air and the wet-heat drawing were both set at 1.0. In the wet-heat drawing, washing and removal of the solvent of the fiber itself were concomitantly carried out, and then the fiber was soaked in a 1.0% by mass solution of aminosilicone-based oiling agent and dried and densified with a heating roller set at 175°C.

[0056]

Subsequent to the above described drying and densifying step, drawing was carried out in pressurized steam to attain a total drawing magnification of 13 to yield an acrylonitrile-based precursor fiber having a single fiber fineness of 1.2 dtex and a total fineness of 3600 dtex.

[0057]

The acrylonitrile-based precursor fiber thus obtained was subjected to a treatment of heating in air at 220°C to 260°C in such a way that the density became 1.35 g/cm³ with a flame retarding time of 60 minutes and an elongation ratio of -5%, and thus converted into a flame retarded fiber. The flame retarded fiber thus obtained was finally fired in an atmosphere of nitrogen at 1250°C to yield a carbon fiber bundle.

[0058]

Thereafter, the carbon fiber bundle was subjected to an electrolytic oxidation treatment with an electric charge of 30 C/g in a 10% nitric acid as electrolytic solution at 25°C to yield a carbon fiber. The obtained carbon fiber was found to correspond to the above described i). The strand strength of this carbon fiber attained a value of 6.5 GPa, and the interfacial shear strength also attained a sufficient value.

[0059]

(Example 2)

The steps were the same as in Example 1 until just before the electrolytic treatment. In the electrolytic treatment, only the electric charge was altered to 2 C/g. The Rms and S of the carbon fiber thus obtained corresponded to the above described i), but the functional group amounts A, B and C deviated from the conditions. The interfacial shear strength was not particularly excellent, but the strand strength was sufficiently high.

[0060]

(Example 3)

The steps were the same as in Example 1 until just before the electrolytic treatment. In the electrolytic treatment, only the electric charge was altered to 600 C/g. The Rms and S of the carbon fiber thus obtained corresponded to the above described i), but as for the functional group amounts A, B and C, the amounts other than C

deviated from the conditions. The interfacial shear strength was not particularly excellent, but the strand strength was sufficiently high.

[0061]

(Example 4)

The steps were the same as in Example 1, inclusive of the electrolytic treatment conditions, except that the drawing-in-air magnification was set at 1.3 and the wet-heat drawing magnification was set at 2.0. The obtained carbon fiber corresponded to the above described ii). The strand strength attained a value of 6.5 GPa and the interfacial shear strength attained a sufficient value.

[0062]

(Example 5)

The steps were the same as in Example 4 until just before the electrolytic treatment. In the electrolytic treatment, only the electric charge was altered to 2 C/g. The Rms and S of the carbon fiber thus obtained corresponded to the above described ii), but the functional group amounts A, B and C all deviated from the conditions. The interfacial shear strength was not particularly excellent, but the strand strength was sufficiently high.

[0063]

(Comparative Example 1)

The steps were the same as in Example 4 until just before the electrolytic treatment. In the electrolytic treatment, only the electric charge was altered to 600 C/g. The carbon fiber thus obtained did not correspond to any one of the above described i) to iii). The strand strength was as inferior as 4.0 GPa.

[0064]

(Example 6)

The steps were the same as in Example 1, inclusive of the electrolytic treatment conditions, except that the drawing-in-air magnification was set at 1.5 and the wet-heat drawing magnification was set at 1.1. The obtained carbon fiber corresponded to the above described ii). The strand strength attained a value of 6.4 GPa and the interfacial shear strength attained a sufficient value.

[0065]

(Example 7)

The steps were the same as in Example 6 until just before the electrolytic treatment. In the electrolytic treatment, only the electric charge was altered to 2 C/g. The Rms and S of the carbon fiber thus obtained corresponded to the above described ii), but the functional group amounts A, B and C all deviated from the conditions. The interfacial shear strength was not particularly excellent, but the strand strength was sufficiently high.

[0066]

(Example 8)

The steps were the same as in Example 6 until just before the electrolytic treatment. In the electrolytic treatment, only the electric charge was altered to 600 C/g. The Rms and S of the carbon fiber thus obtained corresponded to the above described ii), but as for the functional group amounts A, B and C, only the amount A deviated from the condition. The interfacial shear strength was not particularly excellent, but the strand strength was sufficiently high.

[0067]

(Example 9)

The steps were the same as in Example 1, inclusive of the electrolytic treatment conditions, except that the drawing-in-air magnification was set at 1.5 and the wet-heat drawing magnification was set at 1.7. The obtained carbon fiber corresponded to the above described iii). The strand strength attained a value of 6.4 GPa and the interfacial shear strength attained a sufficient value.

[0068]

(Example 10)

The steps were the same as in Example 9 until just before the electrolytic treatment. In the electrolytic treatment, only the electric charge was altered to 2 C/g. The Rms and S of the carbon fiber thus obtained corresponded to the above described iii), but as for the functional group amounts A, B and C, only the amount A deviated from

the condition. The interfacial shear strength was not particularly excellent, but the strand strength was sufficiently high.

[0069]

(Example 11)

The steps were the same as in Example 9 until just before the electrolytic treatment. In the electrolytic treatment, only the electric charge was altered to 600 C/g. The Rms and S of the carbon fiber thus obtained corresponded to the above described iii), but as for the functional group amounts A, B and C, the amounts other than the amount C deviated from the condition. The interfacial shear strength was not particularly excellent, but the strand strength was sufficiently high.

[0070]

(Comparative Example 2)

The steps were the same as in Example 9 until just before the electrolytic treatment except that the wet-heat drawing magnification was set at 3.0. In the electrolytic treatment, only the electric charge was altered to 600 C/g. The carbon fiber thus obtained did not correspond to any one of the above described i) to iii). The strand strength and the interfacial shear strength were both inferior.

[0071]

(Comparative Example 3)

The steps were the same as in Example 9, except that the wet-heat drawing magnification was set at 3.0. The carbon fiber thus obtained did not correspond to any one of the above described i) to iii). The strand strength and the interfacial shear strength were both inferior.

[0072]

[Table 1]

Table 1

Sample	Drawing-in-air magnification	Wet-heat drawing magnification	Electric charge C/g	Maximum wrinkle depth h nm	Root-mean-square surface roughness Rms nm	Surface area ratio S	Total amount of acidic groups μ eq/g			Amount of carboxyl group μ eq/g			Amount of hydroxy group μ eq/g	Resin-impregnated strand strength GPa	Interfacial shear strength Mpa
							A	B	C	A	B	C			
Example 1	1.0	1.0	30	43	18.0	1.015	35.1	18.0	10.3	6.5	37				
Example 2	1.0	1.0	2	46	17.0	1.020	0.2	0.1	0.0	5.5	28				
Example 3	1.0	1.0	600	42	19.8	1.051	40.9	30.3	15.2	5.7	31				
Example 4	1.3	2.0	30	32	18.0	1.156	15.5	6.7	6.7	6.5	39				
Example 5	1.3	2.0	2	31	15.0	1.140	1.3	0.5	0.4	5.6	29				
Comparative Example 1	1.3	2.0	600	35	17.2	1.285	42.0	23.6	11.6	4.0	26				
Example 6	1.5	1.1	30	32	26.0	1.092	18.0	7.1	7.5	6.4	38				
Example 7	1.5	1.1	2	47	24.0	1.089	0.3	0.1	0.1	5.2	29				
Example 8	1.5	1.1	600	52	29.2	1.099	40.3	10.5	11.2	5.4	32				
Example 9	1.5	1.7	30	65	23.1	1.230	15.0	5.9	4.8	6.4	39				
Example 10	1.5	1.7	2	64	22.6	1.221	0.4	0.2	0.1	5.7	30				
Example 11	1.5	1.7	600	68	25.0	1.269	20.8	10.1	6.8	5.3	31				
Comparative Example 2	1.5	3.0	600	105	41.0	1.293	43.0	5.6	8.2	4.4	29				
Comparative Example 3	1.5	3.0	30	102	40.0	1.291	8.0	1.7	0.1	4.8	26				

[0073]

[Advantage of the Invention]

The carbon fiber of the present invention permits physically and chemically controlling the surface of the carbon fiber, and obtaining a carbon fiber excellent in attainment of the strength as a composite material.

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(54) 【発明の名称】 炭素繊維

(57) 【要約】

【課題】 複合材料としての強度発現性にすぐれた炭素繊維を提供する。

【解決手段】 繊維の長手方向に皺を有する炭素繊維であって、原子間力顕微鏡で測定した最大の皺の深さ h (nm) が $3 < h \leq 100$ 、原子間力顕微鏡で測定した自乗平均面粗さ Rms (nm) が $2 \leq Rms \leq 35$ 、かつ、原子間力顕微鏡で測定した投影面積に対する実表面積の比の値 S が $1.01 \leq S \leq 1.28$ である炭素繊維。

【特許請求の範囲】

【請求項1】 繊維の長手方向に皺を有する炭素繊維であって、原子間力顕微鏡で測定した最大の皺の深さ h (nm)が $3 < h \leq 100$ 、原子間力顕微鏡で測定した自乗平均粗さ Rms (nm)が $2 \leq Rms \leq 35$ 、かつ、原子間力顕微鏡で測定した投影面積に対する実表面積の比の値 S が $1.01 \leq S \leq 1.28$ である炭素繊維。

【請求項2】 前記 Rms および S と、中和滴定で測定した炭素繊維1gあたりの全酸性基量 A ($\mu\text{g当量/g}$)、カルボキシル基量 B ($\mu\text{g当量/g}$)、水酸基量 C ($\mu\text{g当量/g}$)が以下の関係にある請求項1記載の炭素繊維。

i) $2 \leq Rms < 20$ かつ $1.01 \leq S < 1.10$ のとき

$25 \leq A \leq 40$ 、 $15 \leq B \leq 30$ かつ $10 < C \leq 30$

ii) $2 \leq Rms < 20$ かつ $1.10 \leq S \leq 1.28$ 、

または、 $20 \leq Rms \leq 35$ かつ $1.01 \leq S < 1.10$ のとき

$15 \leq A \leq 30$ 、 $5 \leq B \leq 20$ かつ $5 < C \leq 15$

iii) $20 \leq Rms \leq 35$ かつ $1.10 \leq S \leq 1.28$ のとき

$0.5 < A \leq 20$ 、 $0 < B \leq 10$ 、かつ $0 < C \leq 10$

$0.5 < A \leq 20$ 、 $0 < B \leq 10$ 、かつ $0 < C \leq 10$

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開示されていない。つまり、複合材料の強度発現のために、炭素繊維表面の凹凸のような物理的な形態と化学的な性質の両者について、適切にコントロールされた炭素繊維が供給されていないのが実状である。このような事情を背景として、炭素繊維の表面の物理的および化学的形態を、コントロールすることにより複合材料としての強度発現性にすぐれた炭素繊維が強く要望されている。

【0006】

【発明が解決しようとする課題】本発明の目的は、炭素繊維表面の物理的および化学的形態をコントロールすることにより、複合材料としての強度発現性にすぐれた炭素繊維を提供することにある。

【0007】

【課題を解決するための手段】本発明の課題は物理的および化学的に表面状態を精密に制御し、サイズ剤との接着性、マトリックス樹脂との接着性に優れた炭素繊維を提供することにある。

【0008】すなわち本発明は、繊維の長手方向に皺を有する炭素繊維であって原子間力顕微鏡で測定した最大の皺の深さ h (nm)が $3 < h \leq 100$ 、原子間力顕微鏡で測定した自乗平均粗さ Rms (nm)が $2 \leq Rms \leq 35$ 、かつ、原子間力顕微鏡で測定した投影面積に対する実表面積の比の値 S が $1.01 \leq S \leq 1.28$ である炭素繊維である。

【0009】また前記 Rms および S と、中和滴定で測定した炭素繊維1gあたりの全酸性基量 A ($\mu\text{g当量/g}$)、カルボキシル基量 B ($\mu\text{g当量/g}$)、水酸基量 C ($\mu\text{g当量/g}$)が以下の関係にあることが好ましい。

i) $2 \leq Rms < 20$ かつ $1.01 \leq S < 1.10$ のとき

$25 \leq A \leq 40$ 、 $15 \leq B \leq 30$ かつ $10 < C \leq 30$

ii) $2 \leq Rms < 20$ かつ $1.10 \leq S \leq 1.28$ 、

または、 $20 \leq Rms \leq 35$ かつ $1.01 \leq S < 1.10$ のとき

$15 \leq A \leq 30$ 、 $5 \leq B \leq 20$ かつ $5 < C \leq 15$

iii) $20 \leq Rms \leq 35$ かつ $1.10 \leq S \leq 1.28$ のとき

$0.5 < A \leq 20$ 、 $0 < B \leq 10$ 、かつ $0 < C \leq 10$

$0.5 < A \leq 20$ 、 $0 < B \leq 10$ 、かつ $0 < C \leq 10$

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$0.5 < A \leq 20$ 、 $0 < B \leq 10$ 、かつ $0 < C \leq 10$

n m以上より大きい場合、繊維束の収束性が低下し焼成工程後の通過性の悪化さらには毛羽の発生によりコンポジットの性能が逆に低下することがわかった。従って、炭素繊維の繊維軸方向に有する皺は、最大深さ100 nm以下であることが好ましく、80 nm以下であることがより好ましく、70 nm以下が特に好ましい。一方、皺最大深さが小さくなりすぎると樹脂との接着性が悪く十分な強度を得ることができない。従って良好な樹脂との接着性を得ることができる有効な皺の深さは3 nmより大きく、好ましくは10 nm以上、より好ましくは15 nm以上である。

【0011】また、樹脂との接着性を発現するために投影面積に対する実表面積の値は1.01以上1.28を超えない範囲とする。Sの値が1.01未満であると完全平滑なので樹脂との接着性が悪く、1.28を超えると強度と樹脂接着性の両立が困難となる。このような観点からより好ましくは1.01以上1.27以下の範囲である。

【0012】さらに、十分な樹脂との接着性を発現するために、自乗平均面粗さRmsは2 nm以上35 nm以下とする。自乗平均面粗さが2 nm未満であるとコンポジットを形成した際、樹脂との接着性が悪く十分な強度が得られない。また、自乗平均面粗さが35 nmより大きいとコンポジットの強度は低下する。

【0013】以上述べたのは炭素繊維表面の化学的状態の如何に関わらず、高品質のコンポジットを作製する上で炭素繊維に課せられた条件である。一方炭素繊維表面の表面凹凸すなわち物理的状態と化学的状態を適切に制御すれば、更に優れたコンポジットの製造が可能になる。

【0014】表面に存在する官能基でコンポジット性能向上に寄与するものはいくつか考えられる。実例を挙げるとカルボキシル基、フェノール性水酸基などの酸性官能基、クロメン型構造、ピロン様構造の塩基性官能基、環状酸化物などの中性官能基であるが、酸性基が特に効果が顕著で好ましい。また酸性基の中でもカルボキシル基及び水酸基がコンポジット性能に最も影響を与える。

【0015】従来の方法でも表面処理で種々の官能基が導入されていたが、本発明ではこれら官能基の内カルボキシル基及び水酸基をそれぞれ独立に制御することで、従来技術にはない効果を奏する。

【0016】これら酸性基量については、炭素繊維1 gあたりの全酸性基量A (μ 当量/g)が $0.5 < A \leq 40$ 、カルボキシル基量B (μ 当量/g)が $0 < B \leq 30$ かつ水酸基量C (μ 当量/g)が $0 < C \leq 30$ を満たすことが好ましい。全酸性基量がこれより少ないと樹脂との接着性が低下する傾向があるという点で不利であり、多いと炭素繊維の強度が低下する傾向があるという点で不利である。また、カルボキシル基量、水酸基量は上記の範囲が望ましく、この範囲内であると強度と樹脂接着

性の両立について好ましい結果が得られる。

【0017】さらにコンポジットにした時の表面の物理的な性質と化学的な性質のバランスという点から、

i) $2 \leq Rms (nm) < 20$ かつ $1.01 \leq S < 1.10$ のとき、つまり炭素繊維の表面皺が浅く、数少ない状態で表面の凹凸が少ない場合、酸素を含む官能基に関しては、 $25 \leq A \leq 40$ 、 $15 \leq B \leq 30$ 、かつ、 $10 < C \leq 30$ 、

ii) $2 \leq Rms < 20$ かつ $1.10 \leq S \leq 1.28$ 、または、 $20 \leq Rms \leq 35$ かつ $1.01 \leq S < 1.10$ のとき、つまり炭素繊維の表面の表面皺が中程度の深さで、表面の凹凸が中程度の場合、酸素を含む官能基に関しては、

$15 \leq A \leq 30$ 、 $5 \leq B \leq 20$ 、かつ、 $5 < C \leq 15$ 、
iii) $20 \leq Rms \leq 35$ かつ $1.10 \leq S \leq 1.28$ のとき、つまり炭素繊維の表面に深い皺が多く、表面の凹凸が大きい場合、酸素を含む官能基に関しては、 $0.5 < A \leq 20$ 、 $0 < B \leq 10$ 、 $0 < C \leq 10$

の関係を満たすとき、強度発現性が高く好ましい。

【0018】この様に表面形態が物理的、化学的に制御された炭素繊維を用いることで、炭素繊維複合材料の性能が制御できるようになる。炭素繊維の表面形態は炭素繊維複合材料の炭素繊維とマトリックス樹脂との界面接着性に大きく影響し、その界面接着性の大小により炭素繊維複合材料の曲げ強度や引っ張り強度等性能のバランスが変化する。つまり、表面形態の制御により、炭素繊維複合材料に目的、用途に応じた性能を持たせることができるようになるのである。

【0019】さらに本発明の物理的な表面粗さをコントロールしたCFの製造法について、一例により詳細に説明する。ここでは湿式紡糸で製造されたアクリル系プレカーサーを前駆体とする製造例について説明するが、本発明の炭素繊維は何らこのようなアクリロニトリル系に限定されるものではない。レーヨン系、ピッチ系等いずれのものでも使用できる。

【0020】アクリロニトリル系前駆体繊維の原料に用いるアクリロニトリル系重合体の重合方法には、重合体の重合方法は溶液重合、懸濁重合等公知の方法の何れをも採用することができる。重合された重合体から、未反応モノマーや重合触媒残渣、その他の不純物類を極力除くことが好ましい。また、前駆体繊維紡糸での延伸性や炭素繊維の性能発現性等の点から、重合体の重合度は極限粘度(η)が1.0以上2.0以下のものが好ましい。

【0021】次に得られた重合体を溶剤に溶解し紡糸原液とする。溶剤としては、ジメチルアセトアミド、ジメチルスルホキシドおよびジメチルホルムアミド等の有機溶剤や塩化亜鉛、チオシアン酸ナトリウム等の無機化合物の水溶液が使用できるが、繊維中に金属を含有せず、

工程が簡略化される点で有機溶剤が好ましく、その中でもジメチルアセトアミドが最も好ましい。

【0022】紡糸したときに緻密な凝固糸を得るためには、紡糸原液としてある程度以上のポリマー濃度を有するポリマー溶液を使用することが好ましく、ポリマー濃度としては17質量%、さらに好ましくは質量19%以上である。また、通常質量25%以下が好ましい。

【0023】紡糸方法としては、紡糸原液を円形断面を有するノズル孔より凝固浴中に吐出し凝固糸とすることができる。凝固浴は、凝固糸断面形状が実質的に円形になり、かつ、凝固糸引き取りに十分な余裕がある条件になるよう、凝固浴濃度、温度を適宜設定する。実質的に円形とは、断面にくびれがなく、長辺と短辺の比率が1.2以下、さらに好ましくは1.1以下の楕円形状をも含むものである。このような断面形状を有する前駆体繊維を用いると、焼成工程において繊維断面方向に均一に耐炎化、炭素化されるので、より高性能な炭素繊維を得ることができる。

【0024】凝固浴は、紡糸原液に用いられる溶剤を含む水溶液が好適に使用され、含まれる溶剤の濃度を適宜調節する。使用する溶剤によって一般的に異なるが、例えばジメチルアセトアミドを使用する場合、その濃度は好ましくは50~80質量%、より好ましくは60~75質量%である。

【0025】また、凝固浴の温度は、温度が低い方が好ましく通常50℃以下が好ましいが、温度を下げすぎると凝固糸の引き取り速度が低下し生産性が低下する傾向があるという点で不利である。このような観点からさらに好ましくは20℃以上40℃以下である。

【0026】上記凝固糸を好ましくは2.0倍以下、さらに好ましくは1.3倍以下に空中延伸する。かかる空中延伸における延伸倍率の下限値は1.0倍以上である。炭素繊維表面の物理的形態の指標である最大の皺の深さ h 、自乗平均面粗さ $R_m s$ および表面積比 S が本発明で規定する範囲に調整するためには、空中延伸における延伸倍率を1.0倍以上2.0倍以下の範囲とすることが好ましい。2.0倍を超えると炭素繊維にしたときの最大の皺の深さが100nmを超える可能性が出てくる傾向があるという点で不利であり、また投影面積に対する実表面積の比が1.28を超える炭素繊維となる可能性が出てくる傾向があり、コンポジットにしたときの強度が低下する傾向があるという点で不利である。コンポジットとする際の工程通過性の悪化を招き毛羽が発生するため強度が低下するため不利である。

【0027】次いで、沸水中で凝固糸に含まれている溶媒を洗浄しながら湿熱延伸する。このときの延伸倍率は、好ましくは3倍未満、さらに好ましくは2倍以下で延伸する。かかる湿熱延伸における延伸倍率の下限値は1.0倍以上である。また、この延伸方法として、2段以上の多段延伸方法を用いることも可能である。この湿

熱延伸倍率が3倍以上になると炭素繊維にしたときの最大の皺の深さが100nmを超える可能性が出てくる傾向があるという点で不利であり、また投影面積に対する実表面積の比が1.28を超える炭素繊維となる可能性が出てくる傾向があり、コンポジットにしたときの強度が低下する傾向があるという点で不利である。

【0028】さらに延伸浴温度は、単糸同士が融着しない範囲でできるだけ高温にすることが効果的である。この観点から、延伸浴の温度は70℃以上の高温とすることが好ましい。多段延伸の場合は、最終浴を90℃以上の高温にすることが好ましい。

【0029】延伸、洗浄後の繊維は公知の方法によって油剤処理を行う。油剤の種類は特に限定されないが、アミノシリコン系界面活性剤が好適に使用される。

【0030】油剤処理後、乾燥緻密化が行われる。乾燥緻密化の温度は、繊維のガラス転移温度を越えた温度で行う必要があるが、実質的には含水状態から乾燥状態によって異なることもあり、温度は100~200℃程度の加熱ローラーによる方法が好ましい。

【0031】乾燥緻密化後、後延伸を行う。後延伸は、高温の加熱ローラー、熱盤ピン等による乾熱延伸、あるいは加圧スチームによるスチーム延伸等の種々の方式を用いることができる。延伸倍率としては1.1倍以上、さらに好ましくは2.0倍以上である。

【0032】かかるアクリル系前駆体繊維を220~270℃の熱風耐炎化炉を通過せしめて耐炎化繊維を得ることができる。すなわち、乾燥緻密化の前に実施される空中延伸と湿熱延伸とからなる前延伸工程と前記乾燥緻密化の後に実施される後延伸工程と、これら全体として、所定の延伸倍率を達成するように、後延伸工程における延伸倍率は選択される。耐炎化工程における雰囲気については、空気、酸素、二酸化窒素、塩化水素などの各酸化性雰囲気を採用できるが、空気雰囲気の方がコストであり、好ましい。

【0033】以上のようにして得られた耐炎化繊維は、窒素等の不活性雰囲気中で炭素化される。1900℃以下の温度で炭素化することが、炭素繊維の強度発現性の観点から好ましく、下限値は1000℃、好ましくは1200℃である。

【0034】次に化学的に表面状態を制御した炭素繊維を得る方法を説明する。炭素繊維は電解液中で電解酸化処理を施したり、気相、または液相での酸化処理を施したりすることによって酸素を含む官能基を導入し、複合材料における炭素繊維とマトリックス樹脂との親和性、接着性を高めることができる。

【0035】ここでは短時間で酸化処理することができ、酸化処理のコントロールも容易なことから硝酸電解酸化処理での方法についてのみ記載するが、酸化処理に関しては、電解質、処理方法ともに硝酸での電解酸化処理にのみ限られるものではなく、公知のいずれの方法で

もよい。

【0036】電解酸化処理の電解液としては酸性、アルカリ性の何れも採用できる。酸性の電解液に溶存させる電解質の具体例としては、硫酸、硝酸などの無機酸、酢酸、酪酸などの有機酸、硫酸アンモニウム、硝酸アンモニウム、硫酸水素アンモニウムなどの塩が挙げられる。中でも強酸性を示す硫酸、硝酸が好ましい。アルカリ性の電解液に溶存させる電解質の具体例としては、水酸化ナトリウム、水酸化カリウムなどの水酸化物、アンモニア、炭酸ナトリウム、炭酸水素ナトリウムなどの無機塩類、酢酸ナトリウム、安息香酸ナトリウムなどの有機塩類、さらにこれらのカリウム塩、バリウム塩又は他の金属塩、及びアンモニウム塩、水酸化テトラエチルアンモニウム又はヒドラジンなどの有機化合物が挙げられるが、樹脂の硬化障害を防止する観点から、アルカリ金属を含まない炭酸アンモニウム、炭酸水素アンモニウム、水酸化テトラアルキルアンモニウム類が好ましく使用できる。使用する電解質の濃度は1質量%以上50質量%以下が好ましい。また、全酸性基量、カルボキシル基量、水酸基量をコントロールするためにこれらの電解液を2種類以上任意に混合して使用することも可能である。

【0037】さらに、処理温度についても、官能基量の制御に影響するため15℃から80℃の範囲が好ましい。

【0038】処理電解槽においてかける電流値と電流をかける時間、つまり通電する電気量も各官能基の生成量に影響を及ぼす。

【0039】通電する電気量は、炭素繊維の炭化度や使用する塩の種類、濃度に応じて最適化することができる。表層の結晶性の低下を適度に抑える観点から、電気量は3~500クーロン/g、さらには5~200クーロン/gの範囲とするのが好ましい。

【0040】電解酸化処理の後、糸条を水洗及び乾燥するのが良い。乾燥に際しては、温度が高過ぎると炭素繊維の最表面に存在する官能基が熱分解により消失しやすいため、乾燥温度はできる限り低くするのが望ましく、200℃以下で乾燥するのが良い。

【0041】このような方法で得られた炭素繊維を、常法により、マトリックスと組み合わせて、中間基材であるブリブレグや、最終生產品である複合材料とすることができる。マトリックスとして使用する樹脂としては、特に制限はないが、エポキシ樹脂、フェノール樹脂、ポリエステル樹脂、ビニルエステル樹脂、ビスマレイミド樹脂、ポリイミド樹脂、ポリカーボネート樹脂、ポリアミド樹脂、ポリプロピレン樹脂、ABS樹脂などが挙げられる。また、マトリックスには、前記樹脂以外に、セメント、金属、セラミックスなどを使用することもできる。

【0042】

【実施例】以下に、実施例により本発明をより具体的に説明する。なお、各物性値は以下に示す方法で測定した。各測定は複数の試料に対して評価を行いその平均値を採用した。

【0043】また、含有率の表記に用いる「%」は質量%を表すこととする。

【0044】<皺の深さ>評価すべき炭素繊維単糸を数本へモカバークラス上にのせ、両端を接着液(例えば、文具の修正液)で固定したものをサンプルとし、原子間力顕微鏡(セイコーインスツルメンツ製、SPI3700/SPA-300)によりシリコンナイトライド製のカンチレバーDF-20を使用してサイクリックコンタクトモードにて測定を行う。各炭素繊維単糸の任意の2.5μmの範囲を測定し、得られた測定画像は二次元フーリエ変換を行い、炭素繊維表面の曲率、すなわち、緩やかな凹凸変形など相当する低周波成分をカットした後、逆変換を行い、炭素繊維表面の曲率に由来する凹凸をく。前記の処理を施して得られる平面画像について、逆フーリエ変換によって求めた画像では数学的な処理により上下、左右の両端に歪みがあるため、中心部分より2μm四方の画像を取り出し、任意の断面について、表示されている皺の深さを測定する。かかる測定方法で得られた各炭素繊維単糸の表面に存在する複数の皺の中で、最も深い皺を「最大深さの皺」と定義する。

【0045】<自乗平均面粗さ>上記の方法により原子間力顕微鏡により得られた原像について、二次元フーリエ変換を行い、炭素繊維表面の曲率に相当する低周波成分をカットした後、逆変換を行い、炭素繊維表面の曲率に由来する成分を除き、急峻な皺形状のみを表示するものとする。この画像について装置付属のソフトウェアのcross sectionモードにて自乗平均面粗さを測定した。

【0046】<投影面積に対する実表面積の比率:表面積率>上記の方法により原子間力顕微鏡により得られた原像について、二次元フーリエ変換を行い、炭素繊維表面の曲率に相当する低周波成分をカットした後、逆変換を行い、炭素繊維表面の曲率に由来する成分を除き、急峻な皺形状のみを表示するものとする。この画像について装置付属のソフトウェアのcross sectionモードにて投影面積に対する実表面積の比率すなわち表面積率を測定した。

【0047】<全酸性基量、カルボキシル基量、水酸基量>窒素雰囲気下で炭素繊維約1.3gずつを3種類のアルカリ溶液80mlに24時間浸す。各アルカリ溶液について上澄みを取り、5μmのディスクフィルターでろ過した。このそれぞれのアルカリ溶液のろ過液を20ml用いて、10mmol/lの塩酸により電位差滴定を行った。電位差滴定は平沼産業社製COM-550にて行った。また炭素繊維を用いないブランク測定を同時にし、次式により表面官能基量を求めた。なお測定

は3回行い、平均値を採用した。

【0048】CF表面の官能基量 (μ 当量/g) =
 $(\text{サンプルの滴定値 (ml)} - \text{ブランクの滴定値 (ml)}) \times 10 \times \text{アルカリ溶液濃度 (mol/l)} \times f \times 80 / 20 \div \text{使用した炭素繊維重量 (g)} \times 1000$
 $f: 0.01N$ 塩酸のファクター: (キシダ化学 10 mmol/l容量分析用塩酸使用。20°Cのとき1.00)

使用するアルカリ溶液とそれに対して求められる表面官能基は次の通りである。

- ・10 mmol/l 水酸化ナトリウム→カルボキシル基+ラクトン開環によるカルボキシル基+水酸基
- ・5 mmol/l 炭酸ナトリウム→カルボキシル基+ラクトン開環によるカルボキシル基
- ・10 mmol/l 炭酸水素ナトリウム→カルボキシル基

従って、表面の全酸性基量は水酸化ナトリウムの滴定量から、カルボキシル基量は炭酸水素ナトリウムの滴定量から求められる。水酸基量は「水酸化ナトリウムの滴定量から求めた表面官能基量」-「炭酸ナトリウムの滴定量から求めた表面官能基量」から求められる。

【0049】<界面せん断強度>樹脂との接着強度の評価である界面せん断強度は単繊維埋め込み(フラグメンテーション)法により行なった。具体的には例えば、リアライズ社「炭素繊維の展開と評価方法」第157頁~第160頁に記載されている。すなわち、単繊維1本を樹脂中に包埋した試験片を作製し、この試験片に繊維の破断伸度より大きな伸張を付与した。樹脂中で破断した各繊維の長さを読み取ることによって界面せん断強度を算出した。

【0050】

臨界繊維長 (mm) = $4 \times \text{平均繊維長 (mm)} / 3$
 界面せん断強度 (MPa) = 繊維強度 (MPa) \times 繊維直径 (mm) / $2 \times \text{臨界繊維長 (mm)}$

試験片作製に用いた樹脂はCIBA-GEIGY社製「アラルダイドCY230」を100部、「ハードナーHY2967」を35部の割合で混合し、これを専用の型枠に流し込み、20°Cで24時間、60°Cで6時間の温度条件で硬化した。引張試験は室温にて行なった。試験片が破断しない範囲内で(伸度7%)伸張を付与したあと、樹脂内で破断した繊維の長さを偏光顕微鏡で読み取り、平均繊維長を算出した。

【0051】<ストランド強度>ストランド強度はJIS R-7601記載の方法で測定した。

【0052】ストランドの作製は、油化シェル社製「エビコート828」(100部)、無水メチルナジック酸(90部)、ジベンジルジメチルアミン(2部)、アセトン(50部)を混合した組成の樹脂を炭素繊維に含浸後、50°Cで1時間、130°Cに1時間かけて昇温後、130°Cで2時間の条件で硬化させ、樹脂含浸ストラ

ドを得る。得られた樹脂含浸ストランドを用い、樹脂含浸ストランド試験法(JIS R 7601に準拠)により樹脂含浸ストランド引っ張り強度を求めた。

【0053】以下に実施例及び比較例を述べるが、種々のデータを表1にまとめて示した。

【0054】(実施例1)懸濁重合法にて、アクリロニトリル96%、メタクリル酸1%、アクリルアミド3%で共重合したアクリル系共重合体を、ジメチルアセトアミドに溶解して紡糸原液(重合体濃度21%、原液温度60°C)を調整した。この紡糸原液を、直径0.075 mm、孔数3000の口金を用いて、温度38°C、濃度67%のジメチルアセトアミド水溶液に吐出し凝固糸とした。

【0055】この凝固糸を、表1に示す倍率で空气中延伸、続いて、湿熱延伸を施した。空气中延伸倍率及び湿熱延伸倍率共に1.0倍とした。この湿熱延伸の際、併せて、繊維自体の洗浄・脱溶剤が行われ、その後、1.0質量%のアミノシリコン系油剤溶液中に浸漬し、175°Cの加熱ローラーにて乾燥緻密化した。

20 【0056】前記乾燥緻密化工程に引き続いて、加圧水蒸気中でトータル延伸倍率が1.3倍になるように延伸して、単糸織度が1.2 dtex、トータル織度が3600 dtexのアクリロニトリル系前駆体繊維を得た。

【0057】このアクリロニトリル系前駆体繊維を耐炎化時間60分、伸張率-5%で密度1.35 g/cm³となるように空气中220°C~260°Cで加熱処理を施し、耐炎化繊維とした。この耐炎化繊維を最終的に窒素雰囲気中1250°Cの温度で焼成し炭素繊維束を得た。

30 【0058】この後、10%硝酸を電解液とし25°Cで電気量30 C/gで電解酸化処理を行い、炭素繊維を得た。得られた炭素繊維は前記i)に該当するものであった。このストランド強度は6.5 GPaが得られ、界面せん断強度も十分な値であった。

【0059】(実施例2)電解処理直前まで実施例1と同様の工程である。電解処理は、電気量のみ2 C/gに変えた。得られた炭素繊維のRmsとSは前記i)に該当するものであるが、官能基量A、B及びCが条件から外れていた。界面せん断強度は特に優れたものではなかったが、ストランド強度は十分高かった。

40 【0060】(実施例3)電解処理直前まで実施例1と同様の工程である。電解処理は、電気量のみ600 C/gに変えた。得られた炭素繊維のRmsとSは前記i)に該当するものであるが、官能基量A、B、CについてはCを除き条件から外れていた。界面せん断強度は特に優れたものではなかったが、ストランド強度は十分高かった。

50 【0061】(実施例4)空气中延伸倍率を1.3倍及び湿熱延伸倍率を2.0倍にした以外、電解処理条件も含め実施例1と同じである。できた炭素繊維は前記i)に該当するものであった。ストランド強度は6.5

GPaが得られ、界面せん断強度も十分な値であった。

【0062】(実施例5) 電解処理直前まで実施例4と同様の工程である。電解処理は、電気量のみ2C/gに変えた。得られた炭素繊維のRmsとSは前記i i)に該当するものであるが、官能基量A、B、Cについては全て条件から外れていた。界面せん断強度は特に優れたものではなかったが、ストランド強度は十分高かった。

【0063】(比較例1) 電解処理直前まで実施例4と同様の工程である。電解処理は、電気量のみ600 C/gに変えた。得られた炭素繊維は前記i)～i i i)のいずれにも該当しないものであった。ストランド強度は4.0GPaと劣るものであった。

【0064】(実施例6) 空气中延伸倍率を1.5倍及び湿熱延伸倍率を1.1倍にした以外、電解処理条件も含め実施例1と同じである。できた炭素繊維は前記i i)に該当するものであった。ストランド強度は6.4GPaが得られ、界面せん断強度も十分な値であった。

【0065】(実施例7) 電解処理直前まで実施例6と同様の工程である。電解処理は、電気量のみ2C/gに変えた。得られた炭素繊維のRmsとSは前記i i)に該当するものであるが、官能基量A、B、Cについては全て条件から外れていた。界面せん断強度は特に優れたものではなかったが、ストランド強度は十分高かった。

【0066】(実施例8) 電解処理直前まで実施例6と同様の工程である。電解処理は、電気量のみ600C/gに変えた。得られた炭素繊維のRmsとSは前記i i)に該当するものであるが、官能基量A、B、Cについては官能基量Aのみ条件から外れていた。界面せん断強度は特に優れたものではなかったが、ストランド強度は十分高かった。

【0067】(実施例9) 空气中延伸倍率を1.5倍及

び湿熱延伸倍率を1.7倍にした以外、電解処理条件も含め実施例1と同じである。できた炭素繊維は前記i i i)に該当するものであった。ストランド強度は6.4GPaが得られ、界面せん断強度も十分な値であった。

【0068】(実施例10) 電解処理直前まで実施例9と同様の工程である。電解処理は、電気量のみ2C/gに変えた。得られた炭素繊維のRmsとSは前記i i i)に該当するものであるが、官能基量A、B、Cについては官能基量Aのみ条件が外れていた。界面せん断強度は特に優れたものではなかったが、ストランド強度は十分高かった。

【0069】(実施例11) 電解処理直前まで実施例9と同様の工程である。電解処理は、電気量のみ600C/gに変えた。得られた炭素繊維のRmsとSは前記i i i)に該当するものであるが、官能基量A、B、Cについては官能基量Cを除き条件が外れていた。界面せん断強度は特に優れたものではなかったが、ストランド強度は十分高かった。

【0070】(比較例2) 湿熱延伸倍率を3.0倍にした以外、電解処理前までは実施例9と同じである。電解処理は、電気量のみ600C/gに変えた。できた炭素繊維は前記i)～i i i)のいずれにも該当しないものであった。ストランド強度、界面せん断強度とも劣るものであった。

【0071】(比較例3) 湿熱延伸倍率を3.0倍にした以外、実施例9と同じである。できた炭素繊維は前記i)～i i i)のいずれにも該当しないものであった。ストランド強度、界面せん断強度とも劣るものであった。

【0072】

【表1】

表1

サンプル	空気中延 伸倍率	湿熱延 伸倍率	電気量 C/g	最大の縫 の深さ h mm	自乗平均 面粗さ Rms nm	S	全酸性基量 A μeq/g	カルボキ シル基量 B μeq/g	水酸基量 C μeq/g	樹脂含浸 ストランド 強度 GPa	界面せん断 強度 Mpa
実施例1	1.0	1.0	30	43	18.0	1.015	35.1	18.0	10.3	6.5	37
実施例2	1.0	1.0	2	46	17.0	1.020	0.2	0.1	0.0	5.5	28
実施例3	1.0	1.0	600	42	19.8	1.051	40.9	30.3	15.2	5.7	31
実施例4	1.3	2.0	30	32	18.0	1.156	15.5	6.7	6.7	6.5	39
実施例5	1.3	2.0	2	31	15.0	1.140	1.3	0.5	0.4	5.6	29
比較例1	1.3	2.0	600	35	17.2	1.285	42.0	23.6	11.6	4.0	26
実施例6	1.5	1.1	30	32	26.0	1.092	18.0	7.1	7.5	6.4	38
実施例7	1.5	1.1	2	47	24.0	1.089	0.3	0.1	0.1	5.2	29
実施例8	1.5	1.1	600	52	29.2	1.099	40.3	10.5	11.2	5.4	32
実施例9	1.5	1.7	30	65	23.1	1.230	15.0	5.9	4.8	6.4	39
実施例10	1.5	1.7	2	64	22.5	1.221	0.4	0.2	0.1	5.7	30
実施例11	1.5	1.7	600	68	25.0	1.269	20.8	10.1	6.8	5.3	31
比較例2	1.5	3.0	600	105	41.0	1.293	43.0	5.6	8.2	4.4	29
比較例3	1.5	3.0	30	102	40.0	1.291	8.0	1.7	0.1	4.8	26

【0073】

40* 材料としての強度発現性にすぐれた炭素繊維が得られ

【発明の効果】本発明の炭素繊維により、炭素繊維の表面を物理的、化学的に制御することが可能になり、複合*

フロントページの続き

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